

*Anal.*¹² Calcd. for C₁₄H₈Cl₄: C, 51.01; H, 2.64. Found: C, 50.94; H, 2.58.

1,2,3,4,5,6,7,8-Octamethyl-9,10-dihydroanthracene.—In a 200-ml. flask set up as described in the general procedure were placed 14.0 g. (0.05 mole) of bis-(2,3,4,5-tetramethylphenyl)-methane, 4.5 g. (0.15 mole) of paraformaldehyde, and 20 ml. of carbon tetrachloride. A solution of 40 ml. of 96% sulfuric acid in 80 ml. of 95% ethanol was added at 75° to this mixture, which was then stirred vigorously at 80° for 3 hr. The upper layer was then decanted, and the carbon tetrachloride slurry was filtered. The solid was stirred with methanol and again filtered. After two more washings with methanol, the solid was dissolved in 400 ml. of hot xylene and 2 g. of charcoal (Norite A) was added. The mixture was filtered while hot, the filtrate was concentrated to 200 ml., and slowly cooled to effect crystallization.

The compound was converted to 1,2,3,4,5,6,7,8-octamethylanthracene by selenium dehydrogenation as previously described.¹⁰ The removal of selenium from the product was facilitated by repeated treatment of the hot chlorobenzene solution with charcoal. An attempt was made to prepare 1,2,3,4,5,6,7,8-octamethyl-9,10-dihydroanthracene directly from 1,2,3,4-tetramethylbenzene without isolating the intermediate diarylmethane. The product obtained in this way melted at 263–274°. It contained a large amount of impurities which were difficult to remove by recrystallization.

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Allylic Chlorides. XIV. The Preparation and Properties of *cis*- and *trans*-1,2,3-Trichloro-2-butene¹

BY LEWIS F. HATCH AND JOHN J. D'AMICO

The following five new compounds have been synthesized and characterized: *cis*-1,2,3-trichloro-2-butene, *trans*-1,2,3-trichloro-2-butene, *cis*-2,3-dichloro-2-buten-1-ol, *trans*-2,3-dichloro-2-buten-1-ol and 2,3,3-trichloro-1-butene. The relative reactivities of *cis*- and *trans*-1,2,3-trichloro-2-butene and 2,3,3-trichloro-1-butene have been determined for their reaction with potassium iodide in acetone, and with sodium ethoxide in ethanol. Also the relative reactivities of *cis*- and *trans*-2,3-dichloro-2-butene have been determined for their reaction with sodium ethoxide in ethanol. During the course of preparing some of these compounds, unexpected results were obtained. When 2,3,3-trichloro-1-butene was treated with lithium aluminum hydride, only one product was obtained: *trans*-2,3-dichloro-2-butene. When the same compound was treated with an aqueous solution of sodium carbonate, three products were obtained: *cis*- and *trans*-2,3-dichloro-2-buten-1-ol and *trans*-1,2,3-trichloro-2-butene. The apparent allylic rearrangement with lithium aluminum hydride has not been noted previously.

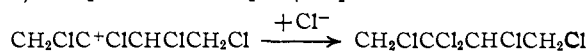
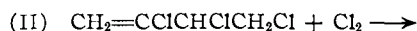
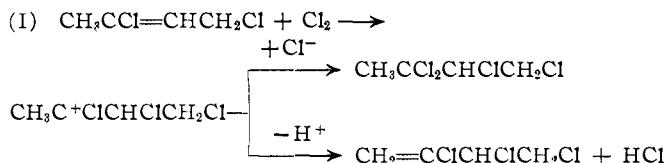
Within recent years a number of allylic chlorides have been synthesized, their structures determined and their properties studied, especially in respect to the influence of geometrical configuration upon relative reactivity.² Two pairs of related geometrical isomers which have received particular attention are the crotyl chlorides^{2,3} (the 1-chloro-2-butenes) and the 1,3-dichloro-2-butenes.⁴ The present paper reports an extension of this study to include the 1,2,3-trichloro-2-butenes.

The diagram illustrates the method used in the preparation of these trichlorides from 1,2,3,3-tetrachlorobutane. The corresponding dichloro alcohols were also prepared from the ethyl α,β,γ -trichlorocrotonates by treatment with lithium aluminum hydride.

In the first method of preparation the 1,2,3,3-tetrachlorobutane which was later dehydrochlorinated to give the desired 1,2,3-trichloro-2-butene was prepared by the addition of chlorine to 1,3-dichloro-2-butene.⁵ The major product of this reaction was 1,2,3,3-tetrachlorobutane but 2,3,4-trichloro-1-butene and 1,2,2,3,4-pentachlorobutane were also formed. It is probable that both the trichloride and the tetrachloride arose from a common intermediate.

This type of reaction mechanism has been proposed to account for the formation of 1,2,3-tri-

chloro-2-methylpropane and 3-chloro-2-chloro-methyl-1-propene, among other compounds, when



methallyl chloride is treated with chlorine under similar conditions.⁶ Carothers and Berchet⁵ have given a somewhat similar reaction mechanism involving a chlorine-olefin complex to explain the products formed during the chlorination of 1,3-dichloro-2-butene. The ratio of addition to substitution in both reaction I (68% addition) and in reaction II (100% addition) is in accord with the generalizations of Taft.⁷

The *trans*-1,2,3-trichloro-2-butene (*trans* in respect to the chlorine atoms on the number 2 and number 3 carbon atoms) obtained by the dehydrochlorination of 1,2,3,3-tetrachlorobutane was treated with lithium aluminum hydride⁸ and *trans*-2,3-dichloro-2-butene⁹ was the only product. The same trichloride was also hydrolyzed by a sodium carbonate solution to give *trans*-2,3-dichloro-2-buten-1-ol.

(1) Presented in part at the 118th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

(2) For paper number XIII of this series see L. F. Hatch and S. S. Nesbitt, *THIS JOURNAL*, **73**, 358 (1951).

(3) L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950).

(4) L. F. Hatch and S. G. Ballin, *ibid.*, **71**, 1039, 1041 (1949).

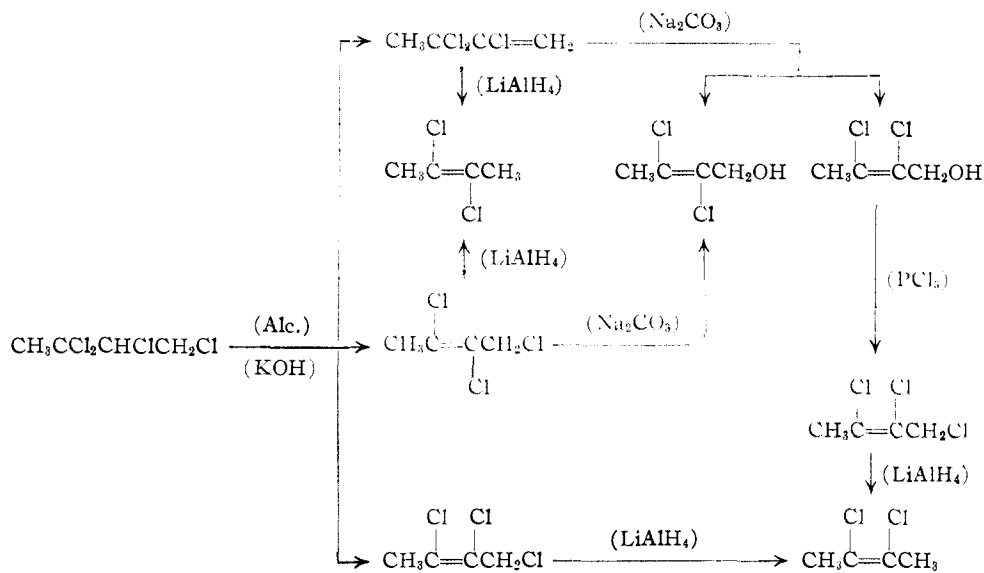
(5) W. H. Carothers and G. J. Berchet, *ibid.*, **55**, 1628 (1933).

(6) J. Burgin, G. Hearne and F. F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

(7) R. W. Taft, *THIS JOURNAL*, **70**, 3364 (1948).

(8) L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

(9) D. V. Tishchenko and A. Churbakov, *J. Gen. Chem. (U. S. S. R.)*, **6**, 1553 (1936).

Preparation of *cis*- and *trans*-1,2,3-trichloro-2-butene.

trans-2,3-Dichloro-2-butene was also the only product when 2,3,3-trichloro-1-butene was treated with lithium aluminum hydride. This apparent allylic rearrangement with lithium aluminum

hydride has not been noted previously. If a free carbonium ion is an intermediate in this reaction it would be expected that both *cis*- and *trans*-2,3-dichloro-2-butene would be formed unless the

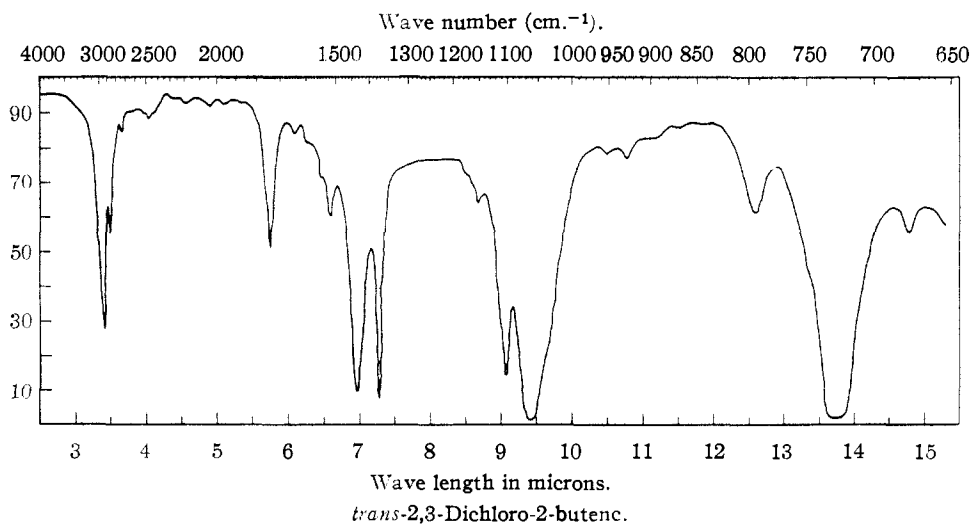
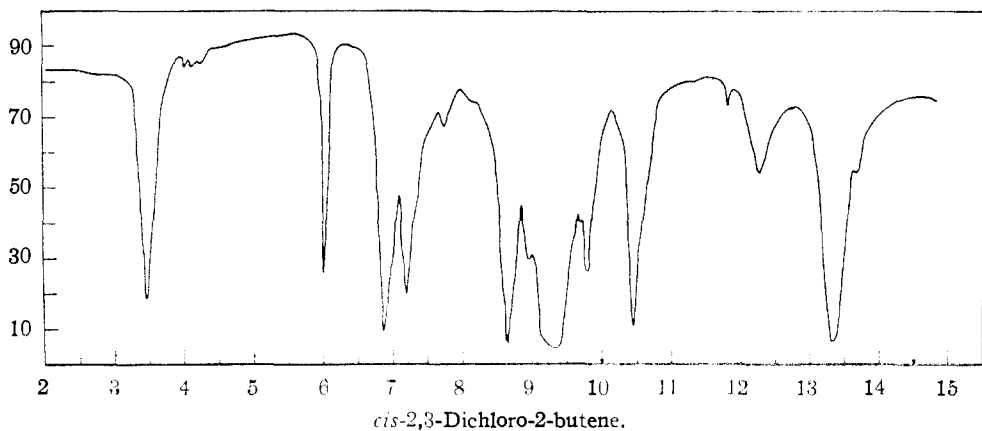


Fig. 1a.

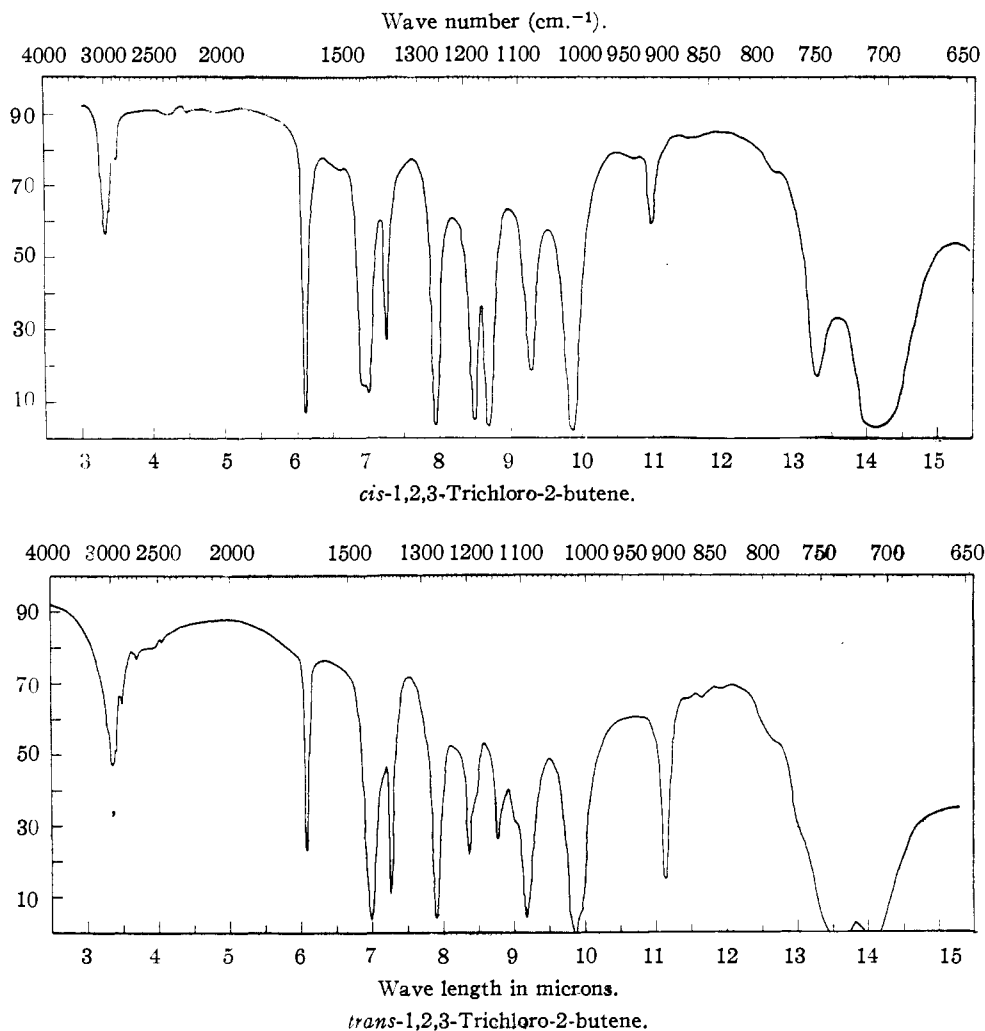


Fig. 1b.

AlH_4^- ion¹⁰ or the trichloride offer steric hindrance which permits the formation of only *trans*-2,3-dichloro-2-butene. Sodium carbonate hydrolysis of 2,3,3-trichloro-1-butene on the other hand gave both *cis*- and *trans*-2,3-dichloro-2-buten-1-ol by allylic rearrangement. The *trans*-alcohol had the same physical properties as the *trans*-alcohol produced by the hydrolysis of *trans*-1,2,3-trichloro-2-butene.

The *cis*-dichloro alcohol was converted to *cis*-1,2,3-trichloro-2-butene by the action of phosphorus trichloride in pyridine. The *cis*-1,2,3-trichloro-2-butene was in turn converted to *cis*-2,3-dichloro-2-butene⁹ by lithium aluminum hydride. By this series of reactions the configuration was established for both the *cis*-1,2,3-trichloro-2-butene and the *cis*-2,3-dichloro-2-buten-1-ol from which it was prepared.

The fraction boiling in the *cis*-1,2,3-trichloro-2-butene range obtained from the dehydrochlorination of 1,2,3,3-tetrachlorobutane was not pure *cis*-1,2,3-trichloro-2-butene for on treatment with lithium aluminum hydride only a 20% yield of *cis*-2,3-dichloro-2-butene was obtained. The un-

reacted material had different physical properties than *cis*-1,2,3-trichloro-2-butene and it is thought that this material may be either α - or β -1,3,3-trichloro-1-butene or a mixture of the two.

The preparation of the isomeric 2,3-dichloro-2-buten-1-ols from the ethyl α,β,γ -trichlorocrotonates (starting with chloroacetic acid) offered neither unexpected difficulties nor products. In every reaction where two geometrical isomers could be formed both isomers were obtained with the *cis*-isomer always being present in the larger amount. It is possible to prepare the 2,3-dichloro-2-buten-1-ols from chloroacetic acid but because of the low yields, especially for the *trans* isomer, it is better to use the method starting with 1,2,3,3-tetrachlorobutane (from 1,3-dichloro-2-butene).

The infrared spectra (Fig. 1) have been obtained from all of the compounds characterized in this study and are in agreement with the proposed configurations.

The relative reactivity with potassium iodide in acetone and sodium ethoxide in ethanol of various chlorides prepared during this investigation are given in Table I. The reaction of *cis*- and *trans*-1,2,3-trichloro-2-butene with potassium iodide shows the anticipated increased reactivity resulting

(10) L. W. Trevo and W. G. Brown, THIS JOURNAL, 71, 1675 (1949).

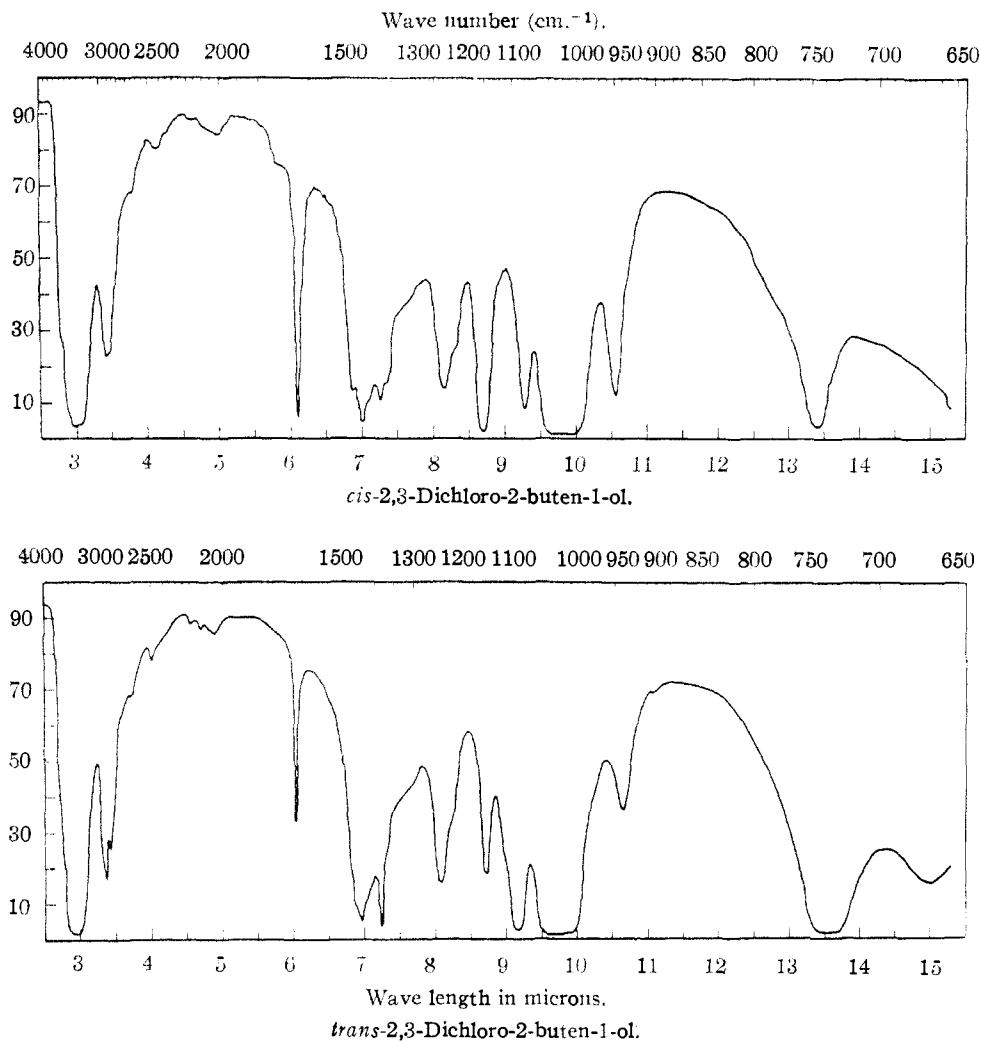


Fig. 1c.

from the replacement of the hydrogen atoms on the number 1 and the number 2 carbon atoms of allyl chloride by a methyl group and chlorine atom.¹¹ The influence of geometrical configuration is also of approximately the same magnitude as previously noted.² These same isomeric trichlorides also show the expected enhanced reactivity toward sodium ethoxide and the usual lack of dependency of reactivity upon configuration.¹² The two isomers of 2,3-dichloro-2-butene have similar reactivities with sodium ethoxide and in the same order of magnitude as those reported by Smith and King^{12c} for the 1,2-dichloro-1-propenes.

The data for the reaction between 2,3,3-trichloro-1-butene and both potassium iodide and sodium ethoxide were obtained at a time when this compound was thought to be *cis*-1,2,3-trichloro-2-butene. The reactivities indicated, however, that the compound did not contain a primary allylic chlorine atom and the infrared spectra indicate the presence of the =CH₂ group. These data plus the elemental analysis and source of the material

(11) L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

(12) (a) L. J. Andrews and R. E. Kepner, *ibid.*, **70**, 3456 (1948);

(b) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949); (c) H. A. Smith and W. H. King, *ibid.*, **72**, 95 (1950).

all tend to confirm the present assignment of structure.

Acknowledgment.—This research was supported by Task 2 funds of the Defense Research Laboratory, The University of Texas, operating under Contract NOrd-9195, Bureau of Ordnance of the Navy Department. The infrared spectra were obtained through the courtesy of R. E. Kitson and the Polychemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

Experimental

The 1,2,3-Trichloro-2-butenes from 1,2,3,3-Tetrachlorobutane. **Preparation of 1,2,3,3-Tetrachlorobutane.**—This tetrachloride was obtained by the addition of chlorine to 1,3-dichloro-2-butene¹³ between 45 and 65° in a manner similar to that used by Carothers and Berchet.⁵ The following yields were obtained: 2,3,4-trichloro-1-butene, 7.1%; 1,2,3,3-tetrachlorobutane, 61.0%; 1,2,2,3,4-pentachlorobutane, 20.9%.

Dehydrochlorination of 1,2,3,3-Tetrachlorobutane.—The 1,2,3,3-tetrachlorobutane (7.30 moles) was dehydrochlorinated by the slow addition of 7.30 moles of solid potassium hydroxide to the tetrachloride in 1650 g. of ethyl alcohol. After the addition of the potassium hydroxide, the reaction mixture was refluxed for five hours. The products were

(13) Furnished by E. I. du Pont de Nemours and Co., Wilmington, Delaware.

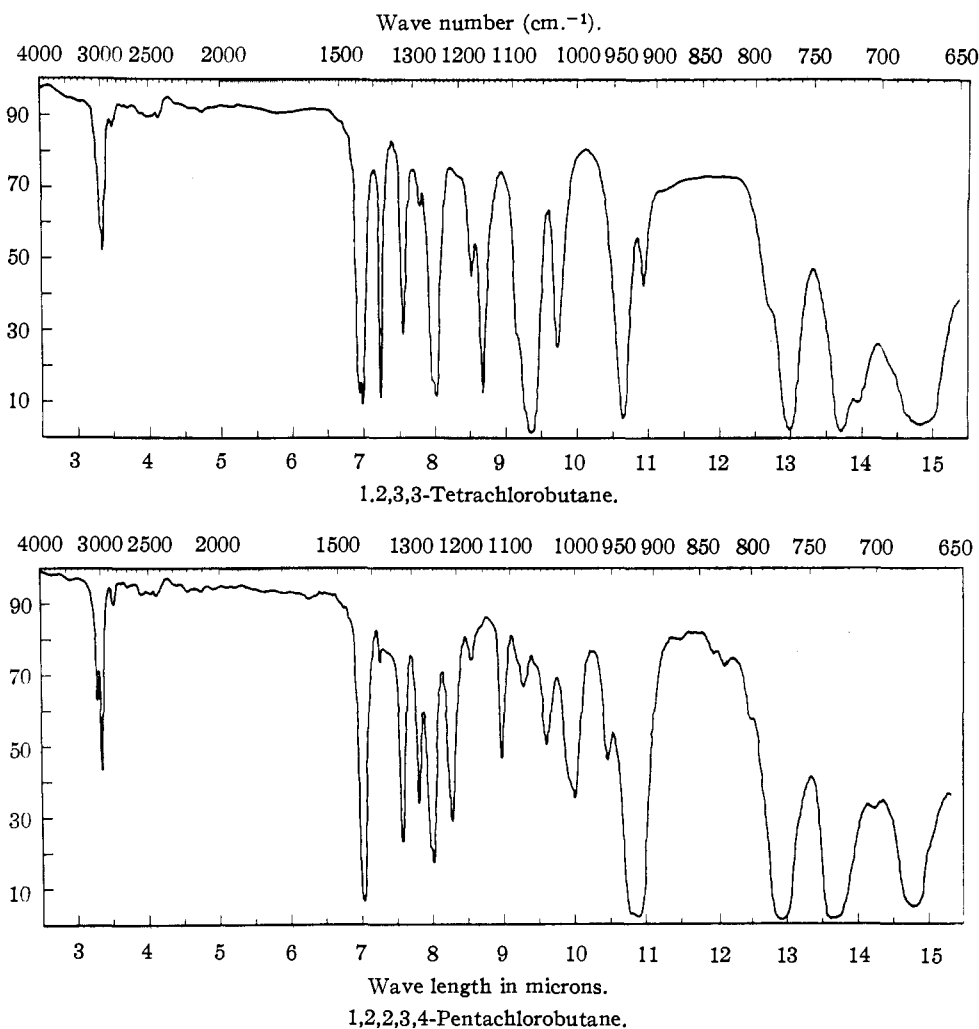


Fig. 1d.

worked up in the usual manner, dried over sodium sulfate and distilled at 30 mm. pressure through the 4-ft. column. The following fractions were obtained:

Compound	B.p., °C. (30 mm.)	n_D^{20}	Yield, %
2,3,3-Trichloro-1-butene	46-67	1.4810	34.5
<i>trans</i> -1,2,3-Trichloro-2-butene	66-67	1.4988	24.9
Cut 4	80-81	1.4980	8.8
1,2,3,3-Tetrachlorobutane (unreacted)	86-87	1.4958	6.7

2,3,3-Trichloro-1-butene.—B.p. 47° (30 mm.); n_D^{20} 1.4815; d_4^{20} 1.3067.

*Anal.*¹⁴ Found: Cl, 66.4, 66.5. Calcd.: Cl, 66.7.

***trans*-1,2,3-Trichloro-2-butene.**—B.p. 66-67° (30 mm.); n_D^{20} 1.4988, n_D^{25} 1.4960; d_4^{25} 1.3329.

*Anal.*¹⁴ Found: Cl, 66.5, 66.7. Calcd.: Cl, 66.7.

Reaction of *trans*-1,2,3-Trichloro-2-butene with Lithium Aluminum Hydride.—*trans*-1,2,3-Trichloro-2-butene (0.214 mole) was treated with lithium aluminum hydride (0.25 mole) in diethyl ether under reflux for five hours. The reaction was carried out in a manner similar to that described by Hatch and Perry.⁸ A 71% yield was obtained of *trans*-2,3-dichloro-2-butene which had the following physical constants: b.p. 100-101° (750 mm.), 41-42° (100 mm.); n_D^{20} 1.4578, n_D^{25} 1.4550; d_4^{20} 1.1418 (lit.⁹ b.p. 101-103° (753 mm.); n_D^{20} 1.4539; d_4^{20} 1.1416).

Hydrolysis of *trans*-1,2,3-Trichloro-2-butene.—*trans*-1,2,3-Trichloro-2-butene (1.00 mole) was hydrolyzed at 80° for

25 hours using a 10% solution of sodium carbonate (1.00 mole). The reaction products were worked up in the usual manner and distilled through the 4-ft. column. A 70% yield of *trans*-2,3-dichloro-2-buten-1-ol was obtained.

***trans*-2,3-Dichloro-2-buten-1-ol.**—B.p. 92-93° (30 mm.); n_D^{20} 1.5000, n_D^{25} 1.4980; d_4^{25} 1.3125.

*Anal.*¹⁴ Found: Cl, 50.2, 50.4. Calcd.: Cl, 50.4.

Reaction of 2,3,3-Trichloro-1-butene with Lithium Aluminum Hydride.—2,3,3-Trichloro-1-butene (0.50 mole) was treated with lithium aluminum hydride (0.25 mole) for three hours in the usual manner.⁸ *trans*-2,3-Dichloro-2-butene in a 58% yield was the only product of this reaction. The dichloride had the following physical constants: b.p. 100-101° (750 mm.); n_D^{20} 1.4578, n_D^{25} 1.4543; d_4^{20} 1.1418.

Hydrolysis of 2,3,3-Trichloro-1-butene.—The 2,3,3-trichloro-1-butene (3.04 moles) was hydrolyzed using a 10% sodium carbonate solution at 80° for 24 hours. The reaction products were worked up in the usual manner and after drying over sodium sulfate they were distilled at 30 mm. through the 4-ft. column. The following data were obtained:

Compound	B.p., °C. (30 mm.)	n_D^{20}	Yield, %
<i>trans</i> -1,2,3-Trichloro-2-butene	66	1.4960	13.0
<i>trans</i> -2,3-Dichloro-2-buten-1-ol	92	1.4980	36.6
<i>cis</i> -2,3-Dichloro-2-buten-1-ol	107-108	1.5035	33.6

A small amount of ketone (probably $\text{CH}_3\text{C}(\text{Cl})=\text{CH}_2$) also appeared to have been formed.

(14) E. Chablay, *Ann. chim.*, 1, 510 (1914).

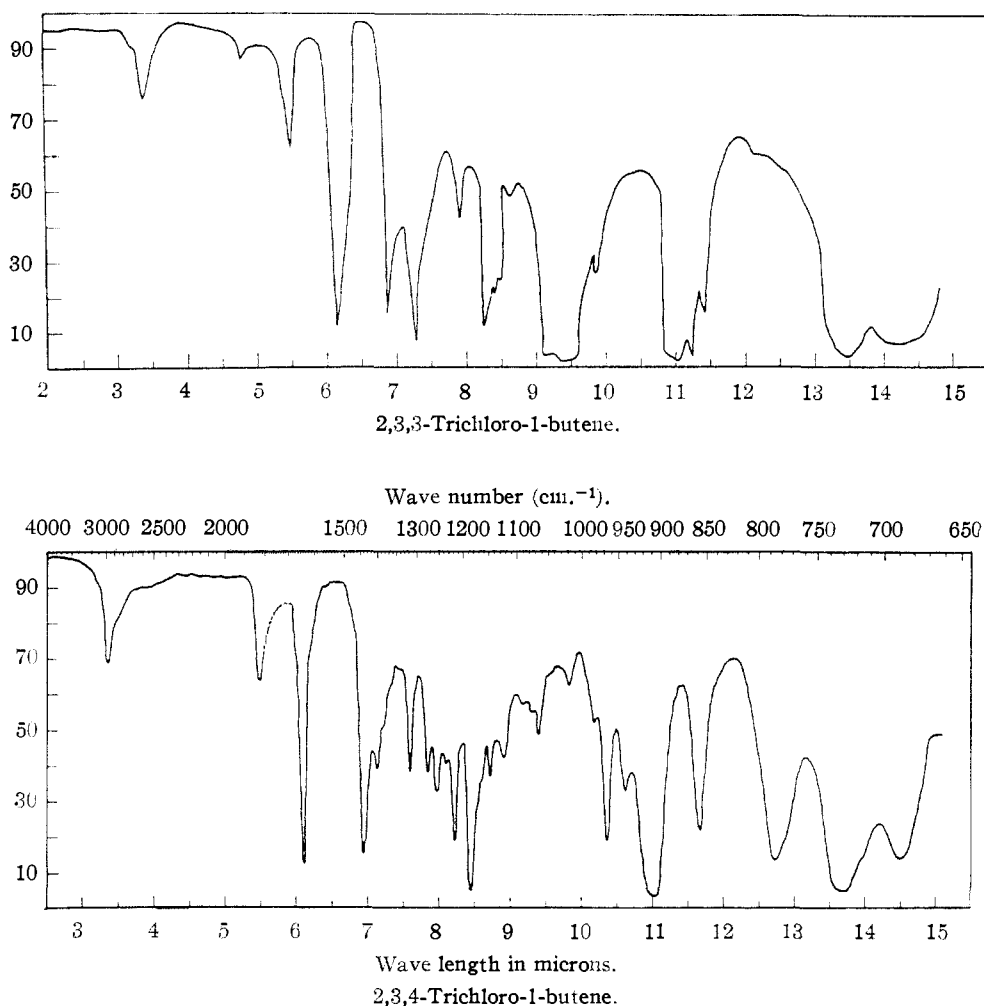


Fig. 1e.

cis-2,3-Dichloro-2-buten-1-ol.—B.p. 107–108° (30 mm.); n_D^{20} 1.5055, n_D^{25} 1.5035; d_4^{25} 1.3315.

*Anal.*¹⁴ Found: Cl, 50.3, 50.6. Calcd.: Cl, 50.4.

cis-1,2,3-Trichloro-2-butene.—*cis*-1,2,3-Trichloro-2-butene (0.63 mole) was prepared by the reaction between the corresponding dichloro alcohol and phosphorus trichloride in pyridine. The procedure was the same as previously described for the preparation of the crotyl chlorides from the crotyl alcohols.⁸ An 80% yield of *cis*-1,2,3-trichloro-2-butene was obtained.

cis-1,2,3-Trichloro-2-butene.—B.p. 80° (30 mm.); n_D^{20} 1.5060, n_D^{25} 1.5039; d_4^{25} 1.3513.

*Anal.*¹⁴ Found: Cl, 66.4, 66.5. Calcd.: Cl, 66.7.

Reaction of *cis*-1,2,3-Trichloro-2-butene with Lithium Aluminum Hydride.—The treatment of 0.19 mole of *cis*-1,2,3-trichloro-2-butene with 0.25 mole of lithium aluminum hydride in the usual manner gave a 72% yield of *cis*-2,3-dichloro-2-butene which had the following physical constants: b.p. 123–125° (749 mm.); n_D^{20} 1.4660, n_D^{25} 1.4635; d_4^{25} 1.1506, d_4^{30} 1.1399 (lit.⁹ b.p. 124–126° (758 mm.); n_D^{20} 1.4590; d_4^{30} 1.1618).

Reaction of Cut 4 from the Dehydrochlorination of 1,2,3,3-Tetrachlorobutane with Lithium Aluminum Hydride.—Cut 4 from the dehydrochlorination of 1,2,3,3-tetrachlorobutane was thought to contain an appreciable amount of *cis*-1,2,3-trichloro-2-butene. To estimate how much of this trichloride was present, 51 g. of Cut 4 was treated with lithium aluminum hydride (0.25 mole) in the usual manner. A 20% yield of *cis*-2,3-dichloro-2-butene (b.p. 123–125°; n_D^{25} 1.4635) was obtained. The remaining material boiled between 125 and 180° with most of it boiling at 180° (n_D^{25} 1.4820).

The 2,3-Dichloro-2-buten-1-ols from the Ethyl α,β,γ -Trichlorocrotonates. Preparation of the Ethyl α,β,γ -Trichlorocrotonates.—These esters were prepared by known methods from chloroacetic acid with ethyl γ -chloroacetate,¹⁵ ethyl β,γ -dichlorocrotonate,¹⁶ and ethyl $\alpha,\beta,\beta,\gamma$ -tetrachlorobutyrate¹⁷ as intermediates. No attempt was made to separate the isomers. B.p. 98–115° (13 mm.) (mostly between 110–115°; n_D^{25} 1.4900 (lit.¹⁷ low boiling isomer: b.p. 98° (13 mm.); n_D^{25} 1.4824; high boiling isomer: b.p. 113° (13 mm.); n_D^{25} 1.4938).

cis- and *trans*-2,3-Dichloro-2-buten-1-ol.—A mixture of the two isomers of ethyl α,β,γ -trichlorocrotonate (0.27 mole) was treated with lithium aluminum hydride (0.27 mole) using the procedure of Nystrom and Brown.¹⁷ The products were distilled through a 2-ft. glass helix-packed column at 30 mm. pressure and a yield of 10% *trans*-2,3-dichloro-2-buten-1-ol (n_D^{20} 1.4982) and 59% *cis*-2,3-dichloro-2-buten-1-ol (n_D^{20} 1.5050) was obtained.

Infrared Spectra.—The infrared spectra data were obtained in the liquid phase using a Perkin-Elmer Model 21 double-beam spectrometer. Sodium chloride optics were used with a cell thickness of 0.037 mm.

Relative Reactivities

Reaction with Potassium Iodide in Acetone.—The same procedure was used as previously described.¹¹ The usual modified second order equation, $k = 1/4bt \log(5-z)/5(1-z)$, was used and a plot of $\log(5-z)/5(1-z)$ vs. time gave

(15) J. F. Hamel, *Bull. soc. chim., France*, [4] **29**, 390 (1921).

(16) G. Oestermann, *ibid.*, 254 (1949).

(17) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1179 (1947).

TABLE I
 RELATIVE REACTIVITIES OF SEVERAL UNSATURATED CHLORIDES

Reaction with Potassium Iodide in Acetone at 20°					
2,3,3-Trichloro-1-butene					
Time, hr.	42	48	72	96	200
% reacted	28.5	30.5	40.7	49.4	75.6
k hr. ⁻¹ (mole/l.) ⁻¹	0.0171	0.0163	0.0150	0.0156	0.0163
Av. k	0.0160 ± 0.0006				
Relative reactivity ^a	0.07				
<i>cis</i> -1,2,3-Trichloro-2-butene					
Time, hr.		0.083	0.166	0.250	0.333
% reacted		44.7	67.0	80.0	88.0
k hr. ⁻¹ (mole/l.) ⁻¹		15.1	15.0	14.8	15.0
Av. k		15.0 ± 0.1			
Relative reactivity ^a		69			
<i>trans</i> -1,2,3-Trichloro-2-butene					
Time, hr.	0.250	0.416	0.500	0.750	1.00
% reacted	48.3	61.6	65.1	77.3	86.3
k hr. ⁻¹ (mole/l.) ⁻¹	5.80	5.03	4.76	4.56	4.77
Av. k	4.98 ± 0.34				
Relative reactivity ^a	23				
Reaction with Sodium Ethoxide in Ethanol at 50°					
2,3,3-Trichloro-1-butene					
Time, hr.	48	60	72	84	120
% reacted	27.6	33.6	36.6	39.6	48.7
k hr. ⁻¹ (mole/l.) ⁻¹	0.126	0.133	0.126	0.123	0.122
Av. k	0.126 ± 0.003				
Relative reactivity ^o	0.11				
<i>cis</i> -2,3-Dichloro-2-butene					
Time, hr.	120	168	216	300	
% reacted	10.7	14.2	17.9	22.8	
k hr. ⁻¹ (mole/l.) ⁻¹	0.0182	0.0176	0.0181	0.0177	
Av. k	0.0179 ± 0.0003				
Relative reactivity ^b	0.015				
<i>trans</i> -2,3-Dichloro-2-butene					
Time, hr.	96	151	218	270	
% reacted	6.4	9.5	14.5	19.5	
k hr. ⁻¹ (mole/l.) ⁻¹	0.0137	0.0136	0.0146	0.0156	
Av. k	0.0144 ± 0.0007				
Relative reactivity ^b	0.012				
<i>cis</i> -1,2,3-Trichloro-2-butene					
Time, hr.	1.0	2.0	3.0	4.0	6.0
% reacted	27.4	43.6	54.3	61.9	72.4
k hr. ⁻¹ (mole/l.) ⁻¹	7.14	7.08	7.11	7.03	7.08
Av. k	7.09 ± 0.03				
Relative reactivity ^b	5.95				
<i>trans</i> -1,2,3-Trichloro-2-butene					
Time, hr.	1.5	2.0	2.5	4.0	6.0
% reacted	39.6	47.7	52.7	64.2	73.8
k hr. ⁻¹ (mole/l.) ⁻¹	8.10	8.04	7.89	7.74	7.84
Av. k	7.92 ± 0.12				
Relative reactivity ^b	6.66				

^a Allyl chloride as 1.00 with $k = 0.218$. ^b Allyl chloride as 1.00 with $k = 1.19$.

a straight line between 28 and 76% reacted for 2,3,3-trichloro-1-butene, between 43 and 88% reacted for *cis*-1,2,3-trichloro-2-butene and between 48 and 86% reacted for *trans*-1,2,3-trichloro-2-butene. The data are given in Table II.

Reaction with Sodium Ethoxide in Ethanol.—A previously described procedure^{12b} was also used with this reaction and the data were calculated using the rate expres-

sion for a second order reaction. The sodium ethoxide solution was 0.04975 molar for the reaction with *trans*-1,2,3-trichloro-2-butene (0.05408 molar), *trans*-2,3-dichloro-2-butene (0.05218 molar) and 2,3,3-trichloro-1-butene (0.06052 molar) and 0.04284 molar with *cis*-1,2,3-trichloro-2-butene (0.05125 molar) and *cis*-2,3-dichloro-2-butene (0.05420 molar). A plot of $\log b(a-x)/a(b-x)$ vs. time gave a straight line for 2,3,3-trichloro-1-butene between 28 and

40% reacted, for *cis*-2,3-dichloro-2-butene between 11 and 23% reacted and for *trans*-2,3-dichloro-2-butene between 6 and 20% reacted. Because of the very slow rate of reaction, data were obtained only for a relatively low percentage reaction. Straight lines were also obtained for *cis*-1,2,3-

trichloro-2-butene between 27 and 72% reacted and for *trans*-1,2,3-trichloro-2-butene between 40 and 74% reacted. The data are given in Table II.

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The Equilibrium between the *o*-Allenylphenoxide and 2-Benzofurylmethyl Anions

By RUSSELL GAERTNER

Evidence is presented to establish that the product of the reaction of 2-(chloromethyl)-benzofuran with magnesium is *o*-allenylphenol. In addition to giving several reactions typical of its functional groups, this compound undergoes a novel base-catalyzed ring closure under mild conditions to give 2-methylbenzofuran. The data are best correlated by a theory involving an equilibrium between the benzofurylmethyl and *o*-allenylphenoxide anions. This appears to be the first demonstration of such an equilibrium between "aromatic" and acyclic systems.

It was shown recently¹ that 2-thenylmagnesium chloride undergoes rearrangements to give 2-methyl-3-substituted-thiophenes when treated with typical reactants. In an attempt to extend the investigation to 2-furfuryl chloride using the cyclic reactor, only polymeric products resulted before hydrolysis. In the hope that this difficulty could be avoided, the corresponding benzofuran derivative has been investigated, with the unexpected results described in this report.

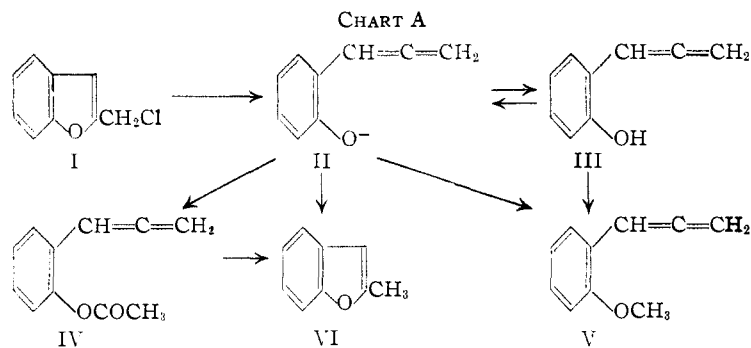
The synthesis of 2-(chloromethyl)-benzofuran (I) allows no uncertainty concerning its structure. Coumarilic acid was reduced with lithium aluminum hydride and the resulting 2-benzofurylcarbinol was converted to the halide by the action of thionyl chloride.

Conversion of the chloride (I in chart A) in the cyclic reactor appeared to proceed normally. However, the ethereal solution failed to yield a carboxylic acid when treated with carbon dioxide. Although its properties suggested that an unsaturated phenol was present, all efforts to isolate this compound were unsuccessful. It polymerized exothermically when simple distillation *in vacuo* was attempted. Even aspiration of solvents at ice temperatures left only a brittle resin. Its unsaturated derivatives also soon polymerized in contact with air but could be distilled and characterized by working rapidly. The phenol (III) was stable in dilute solution in ether or as the anhydrous ethereal magnesium phenoxide (II) prepared in the cyclic reactor.

By hydrogenation of the phenol a 69% yield of *o*-*n*-propylphenol was obtained; its phenylurethan was identical with an authentic sample. The unsaturated phenol was converted by conventional methods to its phenylurethan and acetate (IV). The analytical results and quantitative hydrogenation of both compounds (to derivatives of *o*-*n*-propylphenol) indicated the presence of two double bonds. These facts suggested three possible structures: *o*-propargyl-, *o*-propynyl- or *o*-allenylphenol. Migration of multiple bonds in the presence of bases is well known; however, rearrangement under

such mild conditions to yield a compound in which the unsaturation is not conjugated with the benzene ring would be unprecedented. The choice between the allenyl and propynyl structures was made in part on the basis of an oxidation² with permanganate in pyridine, which produced *no* acetic acid. These data, together with the well-known ease of polymerization of phenylallene, point to the allenylphenol structure, which alone is also consistent with other reactions and the absorption spectra of this series of compounds.

The rearrangement to *o*-allenylphenol might



have been predicted by recognizing that 2-(chloromethyl)-benzofuran is a β -haloether as well as an arylmethyl halide. The cleavage of the former type of compound by reactive metals is the basis for the familiar Boord synthesis³ of olefins. There is an interesting precedent for this scission of the "aromatic" benzofuran nucleus in the observation of Reichstein and Baud⁴ that *o*-ethynylphenol was a product of the reaction of 3-bromobenzofuran with magnesium.

An attempt to methylate *o*-allenylphenol in alkaline solution with dimethyl sulfate led to unexpected results. Although small amounts (13% yield) of *o*-methoxyphenylallene (V) were obtained in this way (when the reaction mixture was cooled),

(2) Young, Ballou and Nozaki, *ibid.*, **61**, 12 (1939). The procedure was originally designed for the analysis of mixtures of allylbenzene and propenylbenzene.

(3) Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); see also Amstutz, *J. Org. Chem.*, **9**, 310 (1944), for a discussion of the mechanism of these reactions and a number of interesting examples.

(4) Reichstein and Baud, *Helv. Chim. Acta*, **20**, 892 (1937). See, concerning the similar behavior of 3-benzofuryllithium, Gilman and Melstrom, *This Journal*, **70**, 1655 (1948).

(1) Gaertner, *This Journal*, **72**, 3934 (1951); *ibid.*, **72**, 4326 (1950).